

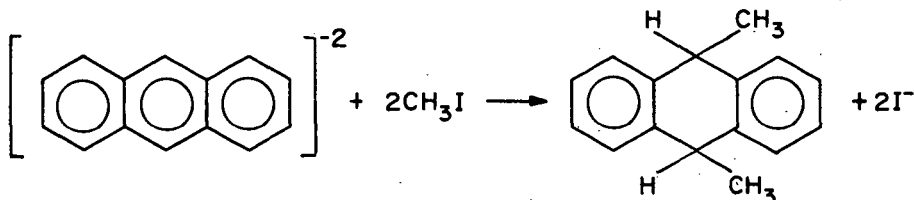
SOLVATION AND REDUCTIVE ALKYLATION OF COAL VIA A "COAL ANION" INTERMEDIATE

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INTRODUCTION

During the last decade a large amount of work has been published on the formation, structure, and reactions of aromatic hydrocarbon anions.^{1,2} These anions are readily formed when aromatic hydrocarbons, dissolved in a suitable solvent, are treated with alkali metals. For example, naphthalene³ dissolved in tetrahydrofuran or hexamethylphosphoramide, $[(CH_3)_2N]_3PO$, reacts with one or two moles of lithium to form the green naphthalene mono-anion, $[C_{10}H_8]^-$ or the red naphthalene di-anion $[C_{10}H_8]^{2-}$ depending on the amount of lithium used. Aromatic hydrocarbon anions react with a wide variety of reagents such as alkyl halides,² carbon dioxide,⁴ acetyl chloride,⁵ aldehydes,⁶ ketones⁶ and compounds containing active hydrogen atoms such as alcohols and water.⁷ For example, anthracene di-anion reacts⁸ with methyl iodide to give among other products 9,10-dimethyl-9,10-dihydroanthracene:



Since coal is believed to contain clusters of condensed aromatic rings, we thought that it might be possible to introduce alkyl groups into the coal molecule by forming aromatic hydrocarbon anions in the coal molecule and then allowing these anions to react with alkyl halides.

EXPERIMENTAL DATA AND RESULTS

Reagents. - Metallic lithium, naphthalene, and hexamethylphosphoramide, (HMPA), were of the highest purity available commercially. Lithium and naphthalene were used as received. HMPA was purified by vacuum distillation and the fraction boiling between 89° and 92° at 4 to 5 mm were used.

Coal. - In all experiments, a hand-picked Pocahontas (lvb) vitrain sample (ground to pass 325 mesh) was used.

Solvation of Coal by Treatment with Lithium in HMPA. - Under a protective cover of nitrogen, 0.1247 gram of vitrain, 0.22 millimole (0.0152 gram) of lithium, and 15 ml of HMPA were placed in a test tube provided with a screw cap. The sealed test tube was gently tumbled (about 40 revolutions per minute) for 8 hours to provide adequate agitation. The contents of the test tube were then centrifuged. The supernatant dark-red solution was pipetted off and the residue treated with 15 ml of HMPA; the resulting suspension was centrifuged and the supernatant solution pipetted off as before. The residue was washed with water until the washings were neutral and the residue was collected on a weighed glass filter. After

drying in vacuo at 100°C, the residue weighed 0.0135 gram, corresponding to 10.8 percent of the original sample. This showed that 89.2 percent of the vitrain was solvated by treatment with lithium in HMPA. By itself, HMPA is only capable of solvating 3 percent of the vitrain.

Alkylation of Naphthalene. - A 1.005 gram sample of naphthalene (7.85 millimoles) and 150 ml of HMPA were placed in a 500 ml Erlenmeyer flask under a protective cover of nitrogen and 0.1328 gram (19.1 millimoles) of lithium wire cut into small pieces was added to the flask. The contents of the flask were stirred by means of a glass enclosed magnetic stirring bar for 8 hours, during which time the color of the solution turned first to a dark green (color of the mono-anion) and then to a dark red (color of the di-anion of naphthalene). The solution was cooled to 5°C and 2.4 ml (30 millimoles) of ethyl iodide was slowly added to the solution with stirring. The reaction mixture was poured into ice water and the aqueous mixture was extracted with pentane. The pentane extract was in turn treated with dilute acid, sodium bicarbonate solution and water to remove any HMPA, and the pentane extract was then freed of pentane. Mass spectrometric and glc analyses of the reaction product indicated that about 30 percent of the naphthalene had been converted to a mixture consisting of di- and tetra-hydro derivatives of mono- and di-methyl and ethyl naphthalene. The main product, on the basis of relative mass peak heights, consisted of equal amounts of ethyl- and diethyldihydro-naphthalene. The reaction product was again alkylated as described above. Analysis of the reaction product from this second alkylation indicated that the overall amount of naphthalene converted was 70 percent, the main product again being ethyl- and diethyldihydronaphthalene.

Alkylation of Coal. - A 1.5290-gram sample of the vitrain (ground to pass 325 mesh) and 150 ml of HMPA were placed in a 500 ml Erlenmeyer flask under a protective cover of nitrogen and 0.2073 gram (29.9 millimoles) of lithium wire was added to the contents of the flask. After the contents of the flask had been stirred for 8 hours, 3 ml (37.5 millimoles) of ethyl iodide was added as described above for the alkylation of naphthalene. The reaction mixture was poured into oxygen-free ice water. The precipitate was washed repeatedly first with water until the washings were neutral and then with ethanol to remove any trace of HMPA. The recovered material, dried in vacuo at 100°, weighed 1.6962 grams and was 35 percent soluble in benzene at room temperature. A 0.4790-gram sample of the recovered coal was again subjected to alkylation with proportional amounts of HMPA and lithium (60 ml and 0.0754 gram, respectively) as described above. The weight of the recovered material was 0.6263 gram and the benzene solubility 86 percent. Table 1 shows the ultimate analysis for the original vitrain, and for the vitrains after the first and second alkylation. Table 2 gives the benzene solubilities of the original and alkylated vitrains at room temperature. Figure 1 shows the infrared spectrum (KBr-pellet) of the original vitrain, that of the vitrain subjected to one and that of the vitrain subjected to two alkylations.

TABLE 1. - Ultimate analysis¹ of alkylated Pocahontas #3 vitrain

	C	H	N	S	O ²	P	I	Ash
Original vitrain	84.85	4.35	1.14	0.63	3.40	0.00	0.00	5.63
First alkylation	82.99	5.92	1.43	.53	4.22	.01	.84	4.06
Second alkylation	81.94	6.69	1.64	.47	3.06	.26	.00	5.94

¹ Dry basis.

² By difference.

TABLE 2. Benzene solubility of original and alkylated Pocahontas vitrain

<u>Vitrains</u>	<u>Percent soluble</u>
Original vitrain	0.5
First alkylation	35.2
Second alkylation	85.8

DISCUSSION

Solvation of Coal, Formation of "Coal Anion"

Although only 3 percent soluble in HMPA, coal becomes almost 90 percent soluble on addition of lithium to a suspension of coal in HMPA. This tremendous increase in solubility on addition of lithium is almost certainly due to the formation of aromatic anions of large volume produced by the transfer of electrons to the coal molecule according to



These negatively charged aromatic clusters probably repel each other and are readily solvated because their charges are distributed over a large volume. The lithium cation on the other hand is effectively solvated by HMPA. Whatever the explanation, the high solubility of the "coal anion" offers an opportunity to introduce alkyl groups into the coal molecule.

Alkylation of Naphthalene

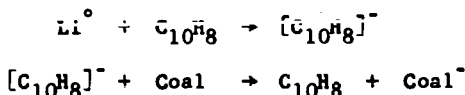
Before attempting to alkylate coal via the "coal anion" in HMPA we explored the feasibility of alkylating a model compound, i.e., naphthalene in this solvent. Treatment of naphthalene with lithium in HMPA produced the dianion $[\text{C}_{10}\text{H}_8]^{-2}$, but alkylation of the di-anion with ethyl iodide yielded in addition to the expected ethyl derivatives also small amounts of methyl derivatives of naphthalene, di- and tetrahydronaphthalene. Apparently, HMPA acted to some extent as a methylating agent under the conditions of our experiment.

Alkylation of Coal

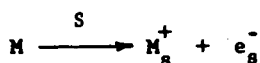
Alkylation of coal with ethyl iodide, carried out by the same procedure as the alkylation of naphthalene, yielded an ethylated coal, which was 35 percent soluble in benzene at room temperature and whose infrared spectrum (KBr-pellet) showed distinct bands (Figure 1) attributable to a methyl group (7.25μ) and its associated stretching vibration (3.4μ). A second alkylation of the recovered coal yielded a product which was now 85 percent soluble in benzene and whose IR spectrum (Figure 1) shows bands of increased intensity at 3.4μ and 7.25μ . A rough estimate of the amount of ethyl groups introduced into the coal may be obtained by assuming that the increase in weight of the recovered material over the starting coal after alkylation is due to the addition of ethyl groups. On the basis of this assumption the amount of ethyl groups introduced into the coal molecule after two alkylations corresponds to about one methyl group per 5 carbon atoms. Some methylation in addition to ethylation of the coal may have taken place in analogy to the reductive ethylation of naphthalene in HMPA described in the experimental part.

Alkylation of Coal in Tetrahydrofuran

Alkylation of coal is not restricted to the use of HMPA. For example, exploratory experiments have shown that coal can be readily alkylated in tetrahydrofuran provided a small amount of naphthalene is added which functions as an electron transfer agent



in the formation of the coal anion. In the case of HMPA, an electron transfer agent is not required since alkali metals readily dissolve in HMPA with formation of solvated cations and solvated electrons according to



where S stands for the solvent, HMPA.^{9,10}

Structure of Coal and of Petroleum Asphaltenes

The fact that introduction of alkyl groups into the coal structure produces a benzene soluble material points to a relationship between alkylated coal and petroleum asphaltenes. The latter are soluble in benzene in spite of the fact that they contain a larger number of rings^{11,12} (8 to 9) per cluster than coal¹² (3 to 4 rings per cluster). However, petroleum asphaltenes, in contrast to coal, contain a considerable number of alkyl groups attached to the aromatic clusters.¹¹ The fact that the introduction of alkyl groups into coal converts coal into a benzene soluble product indicates that the difference between coal and petroleum asphaltenes is not one of molecular size but one of molecular structure.

SUMMARY

Pocahontas (lvb) coal which is only sparingly (3 percent) soluble in hexamethylphosphoramide (HMPA) becomes 90 percent soluble when treated with a solution of lithium in HMPA. This high solubility is probably due to the formation of readily solvated aromatic anions of large volume; these anions are produced by the transfer of electrons from lithium to the aromatic nuclei in coal and readily react with alkylating agents such as ethyl iodide with addition of alkyl groups. The alkylated coal containing approximately one alkyl group per 5 carbon atoms is 86 percent soluble in benzene at room temperature. This method of alkylating coal is a new method for introducing functional groups into the coal molecule, it is not restricted to the use of HMPA as a solvent and should prove useful for modifying the physical and chemical properties of coal. The fact that introduction of alkyl groups into coal converts coal into a benzene soluble material points to a relationship between coal and petroleum asphaltenes and indicates that the difference between coal and petroleum asphaltenes is not one of molecular size but of molecular structure.

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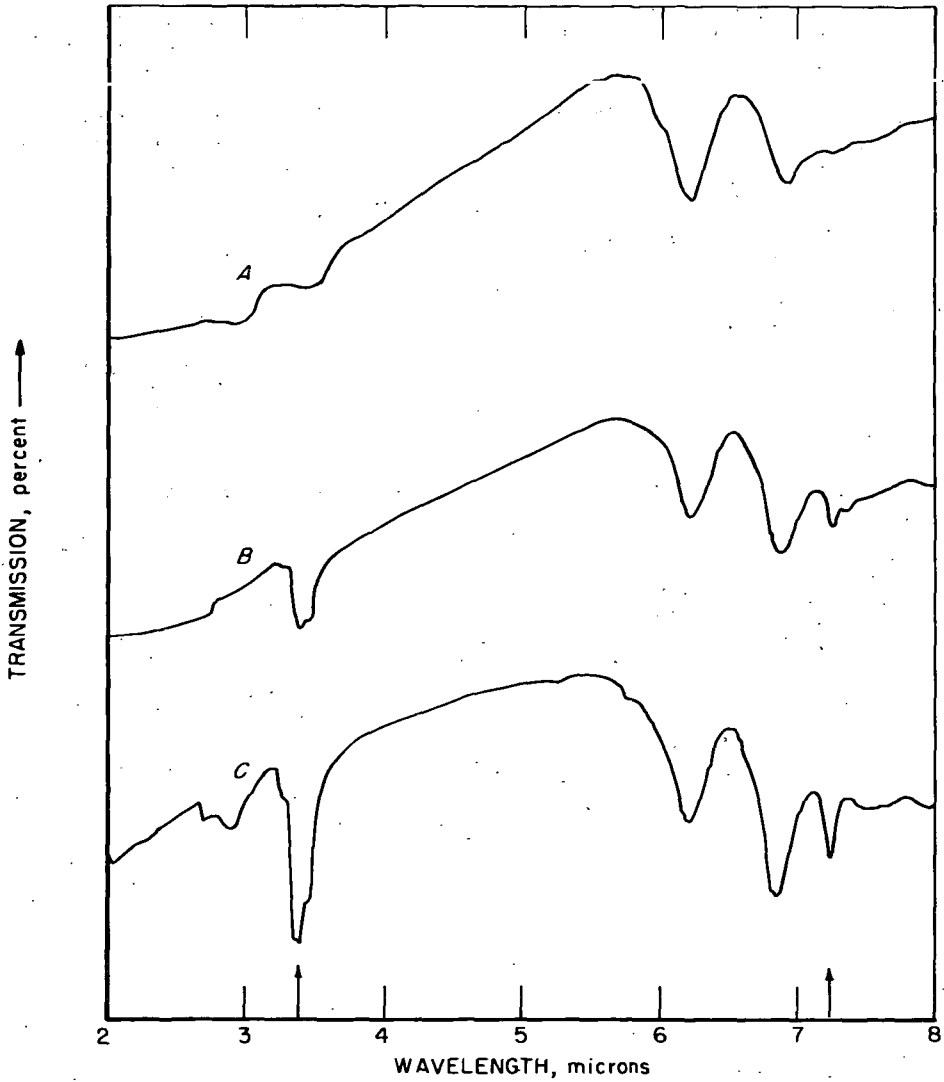


Figure 1.—Spectra of original and alkylated Pocahontas vitrains (A) original, (B) after one alkylation, (C) after two alkylations. Arrows indicate bands attributable to methyl group (7.25 μ) and associated C-H stretching vibration (3.4 μ).

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